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MATERIALS CHEMISTRY AND OPTICAL PROPERTIES OF TRANSPARENT CONDUCTIVE THIN FILMS FOR SOLAR ENERGY UTILIZATION

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ABSTRACT

The science and technology of transparent conductors is discussed in the context of energy applications covering architectural energy-efficient windows, photothermal conversion, and photovoltaics. The overall emphasis is on architectural glazing coatings. Optical properties of heat mirrors are predicted using the Drude theory of metals. Single layer transparent conductors of doped SnO_2, In_2O_3:Sn, and Cd_2SnO_4 are discussed. Detailed materials chemistry is given for spray hydrolysis of SnO_2:F coatings. Multilayer metal/dielectric heat mirrors are covered including basic solar optical properties of metal films. An example system of Al_2O_3/Ag/ polyester heat mirror is also detailed.

Introduction

The science of transparent conductive and semiconductive coatings is of great use to the technological society. The lack of exact relationships between the optical properties of such coatings and their chemical and structural morphology presents a challenge to the chemist and materials scientist. Relationships between deposition conditions and processes need to be better understood to develop conductive coatings with optimum properties.

Transparent conductive materials have a wide variety of potential applications, including solar energy, optics, electro-optics, aerospace, vehicles, lighting, and industrial heat shielding designs. Of the solar energy uses, transparent conductors are important to energy-conserving architectural windows,[1,2a,b] photothermal conversion,[3] photovoltaics,[4,5] and as electrodes in photoelectrochemical cells. The use of transparent conductive coatings as heat mirrors for windows is emphasized in this discourse. However, a brief introduction of both photothermal and photovoltaic uses will be given.

The properties of heat mirror materials important to windows are high solar transmittance, high infrared reflectance (see Fig. 1), chemical and thermal stability. Infrared reflectance is important, since in nontransparent media (as heat mirrors are in the infrared) the spectral properties of reflectance (R, the fraction of incident energy reflected) are related to spectral emittance (E) and absorptance (A, the fraction of incident energy absorbed) by $R = 1 - E$, using Kirchoff's law, $A = E$, at the same wavelength and temperature. Spectral emittance is defined as the ratio of energy emitted by a material to that emitted by a perfect blackbody emitter, both at the same temperature. These relationships imply that a highly reflecting material will have a low emittance at the same wavelength. The lower the emittance the less the magnitude of radiative transfer by the window. By the application of this nearly transparent coating to a window surface, the thermal characteristics can be dramatically altered. Hence, buildings can be more energy efficient. As an example, an optimized triple-glazed window might consist of two outside glass sheets and an inside heat mirror coated sheet. All sheets would be separated and the spaces filled with a low-conductivity gas. The inner sheet could either be polymeric or glass based. The thermal conductivity (U) for such an assembly has been estimated[6] as $U = 0.74\ W/m^2K$. A normal single glazed window has about $U = 6\ W/m^2K$ compared to a nonglass insulated wall of $U = 0.6\ W/m^2K$ (R-11) to $0.3\ W/m^2K$ (R-19). Advanced energy efficient window designs can thus achieve a heat loss rate nearly the same as insulated walls, while still providing view and daylight throughout the year and useful solar gain in the winter to offset heating loads.

The use of a heat mirror coating in a solar collector is to reduce the upward radiative loss from the collecting surface and glazing covers. For this reason, the transparent conductive coating is applied to the inside surface of a single cover or to the top surface of the inside sheet of a double glazing. This coating easily passes high-energy solar radiation (with little absorption) through to the underlying black absorber. This absorber radiates infrared energy at its operative temperature to the covers. The heat mirror coating greatly reduces the radiative heat transfer component and thus reduces the total heat loss from the absorber to the ambient. The net result of this action is to efficiently absorb solar energy and poorly emit infrared energy, much like a selective absorber does. As an example of the heat mirror's significance to a solar collector system, the following demonstration is given. For a system operating at 93°C in an ambient temperature of 21°C, a heat mirror coating is applied to the third surface cover of a double-glazed collector. The absorber is a nonwavelength selective type. The system conversion efficiency is 43 percent compared to 33 percent without the heat mirror.[7] Antireflection coatings can improve this value further. In large solar cavity receivers, system efficiency can increase 20-30 percentage points by using heat mirrors.[8]

For photovoltaics, transparent conductors are optimized for their properties of low sheet resistance, wide bandgap, and high solar transmittance. Transparent conductors have been used as electrical contacts for chemical vapor deposited Cu_2S/CdS cells.[5] Heterojunction cells can be made using transparent conductors in a Schottky barrier configuration. In principle, the highly transparent film acts like a window to couple solar radiation directly into the active substrate. However, it also provides electronic band bending at the barrier-junction necessary for photocurrent production. Furthermore, it serves as an effective antireflection film and top electrical contact. Cells with 14.4 percent efficiency have been reported[9] for In_2O_3:Sn/InP, 12 percent efficiency[10] for In_2O_3:Sn/Si, and 5 percent for SnO_2/Si.[11]

Transparent conductors can be deposited by a variety of methods, including chemical vapor deposition (hydrolysis and pyrolysis reactions), sputtering, vacuum deposition, and plasma-enhanced reactive processes. The thermal and chemical stability limitations of the substrate (glass or polymer) material are very significant to determine which deposition processes can be used. Secondary and competing reactions have to be suppressed by the knowledge of thermodynamic constraints and control of reaction kinetics. The optical properties (solar and infrared) of the substrate influence how effective a coating will be in producing the desired results. The importance of the substrate should not be underestimated when dealing with coating properties.

Theory of Heat Mirrors

Transparent conductors can be classified under two broad categories, single-layer materials such as highly doped SnO_2:F and In_2O_3:Sn, and multilayer metal-based thin films such as SiO_2/Ag, ZnS/Cu/ZnS, and TiO_2/Ag/TiO_2. Both categories are linked by the conductive metal-like properties described by classical Drude theory.[12] In this theory, a well-defined plasma edge is characteristic of the material. It occurs due to excitation of free carriers by incident electromagnetic radiation. Since the charge carriers are actually moving in a potential field of the crystal, an effective mass (m^*) must be used. The $m^* = m_r m_e$, where m_e is the rest mass and m_r is the relative mass of the charge carriers in the field. The complex dielectric constant is related to the optical constants by

$e = e_1 - e_2 = (n - ik)^2$; where $e_1 = n^2 - k^2$ and $e_2 = 2nk$.

For a Drude-like reflector, the dielectric constant can be expressed in terms of (Y/w_p) and (W/w_p) as follows:

$$e_1 = e_b[1 - (1 + (\frac{Y}{w_p})^2) \ / \ ((\frac{W}{w_p})^2 + (\frac{Y}{w_p})^2 \ )] \ ,$$

$$e_2 = e_b[\frac{Y}{w_p} \ (1 + (\frac{Y}{w_p})^2) \ / \ \frac{W}{w_p} \ ((\frac{W}{w_p})^2 + (\frac{Y}{w_p})^2 \ )] \ ,$$

where e_b is the dielectric constant associated with bound carriers (at very high frequency) and Y is the relaxation frequency, $Y = e/um_e$, u is the carrier mobility, and e is the electron charge. The damped plasma frequency is derived as $w_p = (Ne^2/e_b e_o m^*)^{1/2} - Y^2$, and N is the carrier density and e_o is the dielectric constant of air. From this theory, n and k can be extracted in terms of frequency (W). Reflectance (normal-specular) can be derived by $R = ((n-1)^2 + k^2)/((n+1)^2 + k^2)$. The theoretical reflectance for a doped SnO_2 transparent conductor is shown in Fig. 2. The modeled reflectance agrees well with that obtained by experiment. One should note that in the Drude equation as $W >> w_p > Y$, n becomes constant and $k \rightarrow 0$, implying the material is transparent at short wavelengths and for $W << Y < w_p$, $n = k$ are about equal and large in magnitude implying a high reflectance.

Single-Layer Heat Mirrors

Single-layer materials refer mainly to heavily doped oxide semiconductors. Partially transparent metal films are not included in this category since they generally require overcoating films for chemical stability and mechanical durability. The best known transparent semiconductors are In_2O_3:Sn, SnO_2:F, SnO_2:Sb, and Cd_2SnO_4.[1] Characteristic spectral transmission and reflectance values[13-15] are delineated in Fig. 3. It is important to note that these films were made with research apparatus and are the best of their class. Obtaining a reproducible high quality, commercial coating is totally a different matter. Present techniques need to be improved to deposit these coatings on polymeric substrates.

The structural chemistry of SnO_2:F will be developed briefly. This coating is fabricated by spray hydrolysis of stannic chloride over a hot substrate (although other techniques can be used). The overall reaction is as follows:

$$SnCl_4 + 2\ H_2O \rightarrow SnO_2 + 4\ HCl\ .$$

The reaction temperature generally lies between 400–600°C. Substrate reactions such as NaCl formation can restrict the higher reaction temperatures. In place of $SnCl_4$ as a reactant dimethyltin dichloride $(CH_3)_2SnCl_2$ may be used. Doping is achieved by addition of NH_4F. Coatings of SnO_2 electrically conduct by the formation of oxygen lattice defects and atomic substitutional doping. For fluorine doping the chemical substitution reaction is:

$$xF + Sn^{4+}O_2^{2-} \rightarrow \underline{(Sn^{4+} + xe^-)\, O_{2-x}^{2-}\, F_x^-} + xO \, .$$

This equation represents the process where xF^- ions replace a like number of O^{2-} ions. In order to preserve electrical neturality, an additional electron must be accepted from the conduction band to the valence band for each F^-. This, in turn, requires the creation of a hole in the conduction band. For the SnO_2:F film depicted in Fig. 3, typical properties[13] are solar transmittance T_s = 0.75, emittance E(100°C) = 0.15, Electrical Resistivity = 0.67×10^{-3} ohm-cm, N = 5.6×10^{20} cm^{-3}, u = 37 cm^2/V sec, and Y/w_p = 0.14. A similar film has been analyzed by scanning electron microscopy and Auger electron spectroscopy. Partial results are shown in Figs. 4 and 5. The microstructure of this heat mirror consists of a particulate agglomeration with average particle diameter on the order of 0.1 micron. Some chlorine and carbon contamination is noted in the Auger spectrum in Fig. 5a. By sputter depth profiling, it is revealed that the carbon is only at the surface, while chlorine is present throughout as shown in Fig. 5b. An oxygen/tin ratio of 2 is fairly uniform with film depth.

Other promising single-layer materials for transparent conductors are in the groups of rare earth oxides, borides, and transition metal nitrides (as in Fig. 6). Little is known about these materials except that they have electrical conduction with Drude-like behavior.

Multilayer Heat Mirrors

Thin metal films of thicknesses of about 100 Å exhibit partial transparency. The relationship between transmittance and infrared reflectance is depicted in Fig. 7 for several common metals.[16] Generally, metal films have to be overcoated for chemical stability--stability being mainly related to atmospheric oxidation, sulfidization, and corrosion. Also, multilayer coatings can suffer from interdiffusion. Dielectric overcoating materials serve as more than just a protective layer. They are designed to increase the transmittance of the metal film in the solar wavelengths. The dielectric films should have high infrared transparency (no prominent absorption bands) to preserve the metallic infrared reflectance. Example systems[1,17] are SiO_2/M, Al_2O_3/M, and Bi_2O_3/M where M can be Ag, Al, Cu, Au, Ni, etc. Representative three-layer films are[18] TiO_2/M/TiO_2 and ZnS/M/ZnS. Multilayer films can approximate the responses of single-layer transparent conductors (Fig. 3), with the added advantage of wavelength tunability. Metal/dielectric heat mirrors can be fabricated by a variety of processes, including many variants of sputtering and vacuum deposition. Chemical dip coatings can also be used for dielectric deposition.[17] Al_2O_3 deposited from aluminum-alkoxides follow a reaction:

$$Al(OR)_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3\ ROH$$

$$2\ Al(OH)_3 \xrightarrow{T} Al_2O_3 + 3\ H_2O, \quad T = 400\text{–}500^\circ C, \quad R = \text{organic radical.}$$

The microstructure of an ion-beam sputtered Al_2O_3/Ag heat mirror is given in Fig. 8. This particular combination was deposited on polyethylene terephthalate (polyester) film. Use of plastic films can result in lower production costs and weight savings. Their disadvantage is that they cannot withstand many deposition processes due to high temperatures used. The properties of Al_2O_3/Ag shown in Fig. 8 are: Visible transmittance = 0.65, Infrared reflectance = 0.73.

Conclusion

Several types of transparent conductors useful as heat mirrors and their production techniques have been discussed. One of the major obstacles that impede further progress is the need to develop less costly deposition techniques. Coating of flexible plastic substrates is one solution. Lower temperature, atmospheric pressure, and chemical-filming processes need to be devised. Analysis of coatings and understanding of materials chemistry as it relates to coating optical properties and environmental stability is also of high importance.

Acknowledgement

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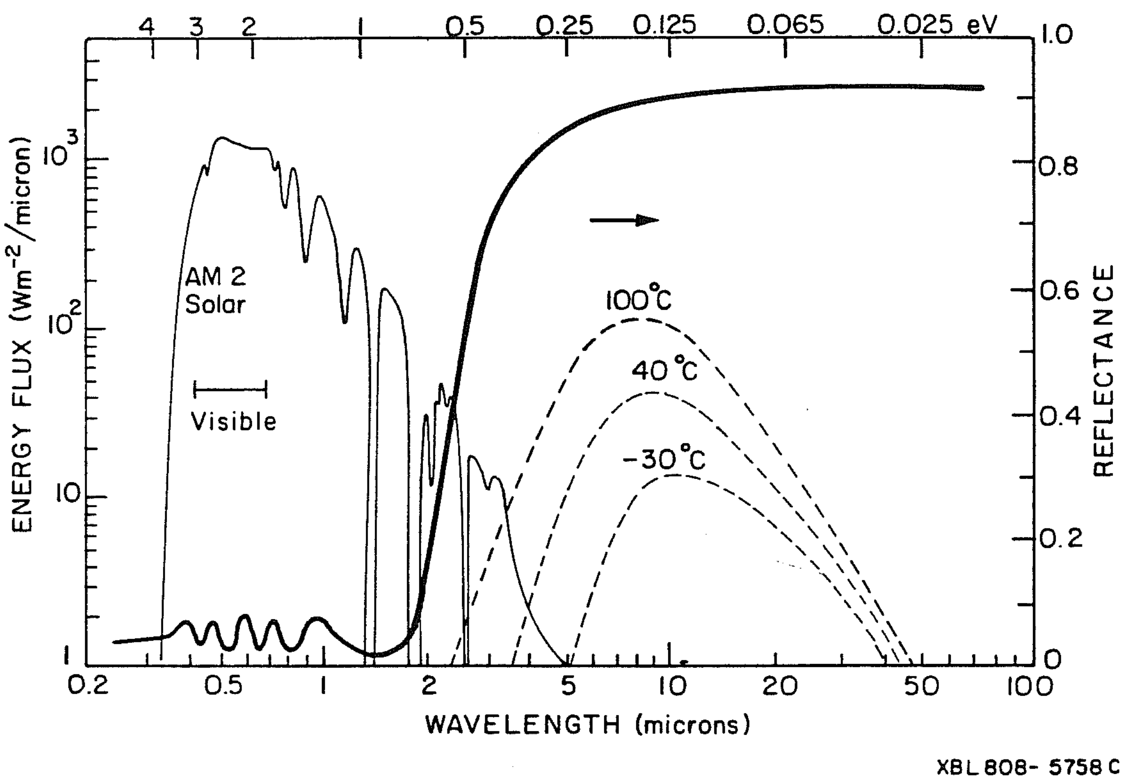

Fig. 1 Spectrum of solar radiation (airmass 2) shown with three blackbody spectral distributions (-30°C, 40°C, 100°C). Superimposed is the idealized selective reflectance of a doped SnO_2 heat mirror coating. The transmission spectrum of this coating is essentially the inverse of the reflectance.

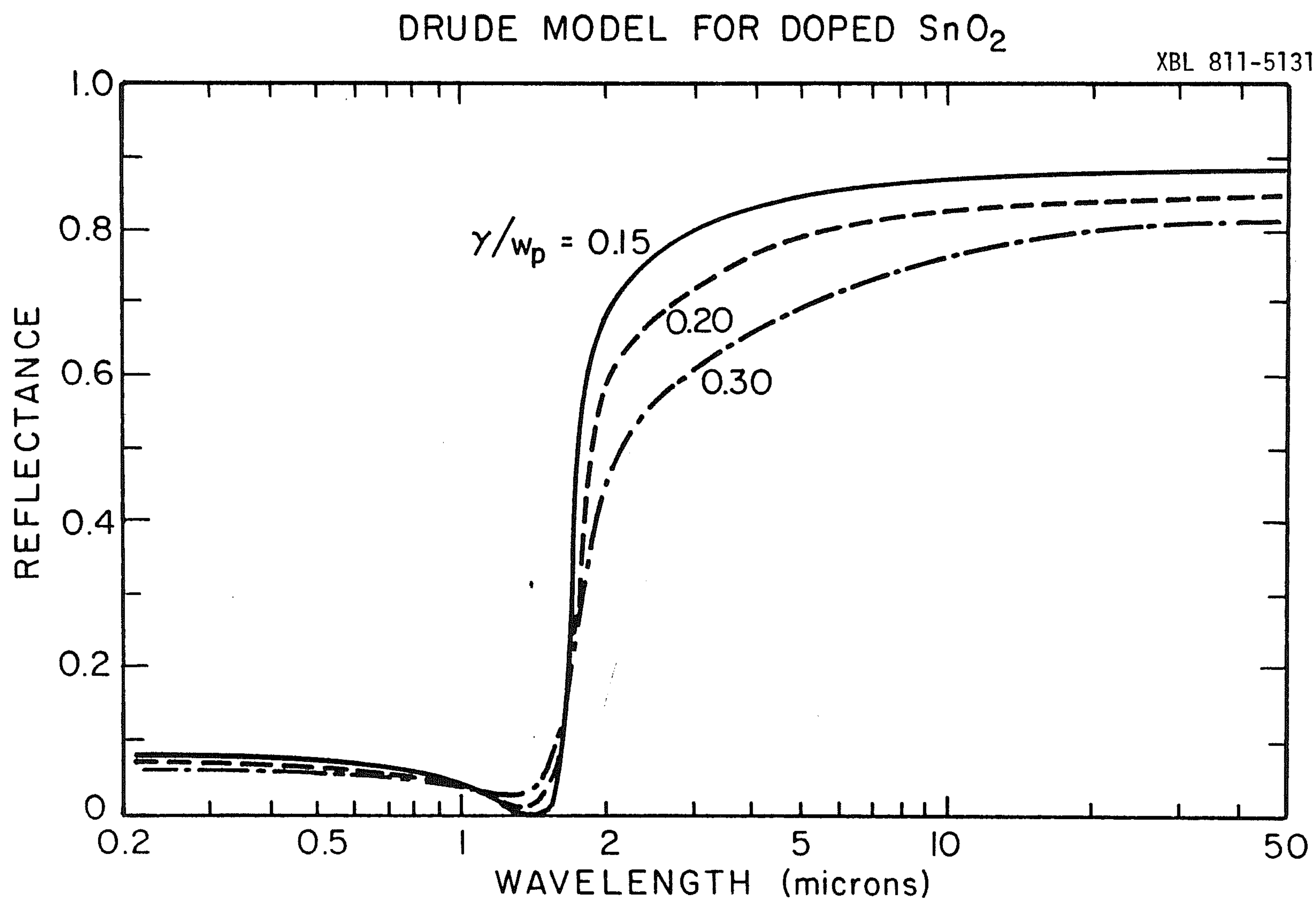

Fig. 2 Drude model for doped SnO_2. Experimental parameters have been used to derive spectral reflectance. Parameters used in the model are dielectric constant = 4, carrier concentration = $5 \times 10^{20} cm^{-3}$, effective mass ratio = 0.3, mobility (a variable) = 17-35 V/cm^2-sec. The ratio of the relaxation frequency to plasma frequency γ/w_p serves as a measure of wavelength selectivity.

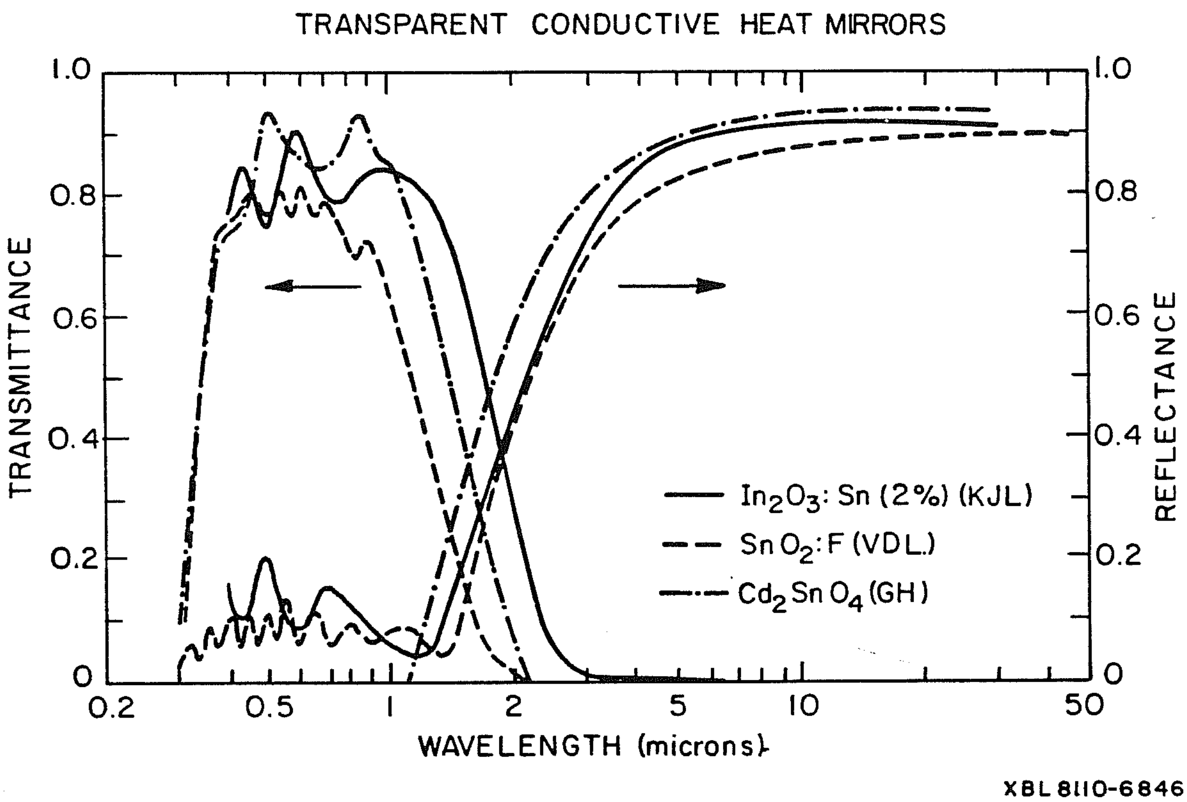

Fig. 3 Spectral normal transmittance and reflectance of heat mirror coatings based on In_2O_3:Sn,[14] Cd_2SnO_4,[15] SnO_2:F.[13]

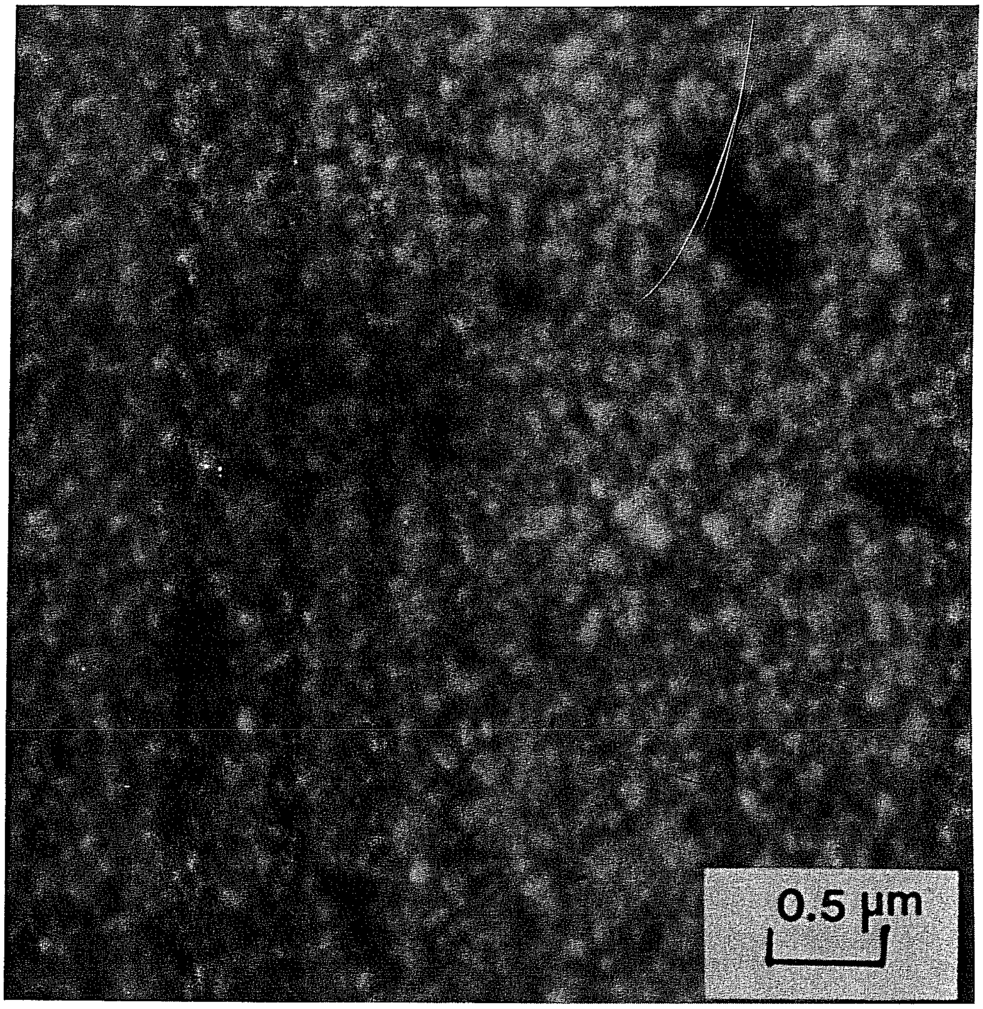

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Fig. 4 Microstructure of an SnO_2:F coating. This coating was made by chemical vapor deposition involving hydrolysis of tin chloride. Sample was analyzed by scanning electron microscopy at 20 kV.

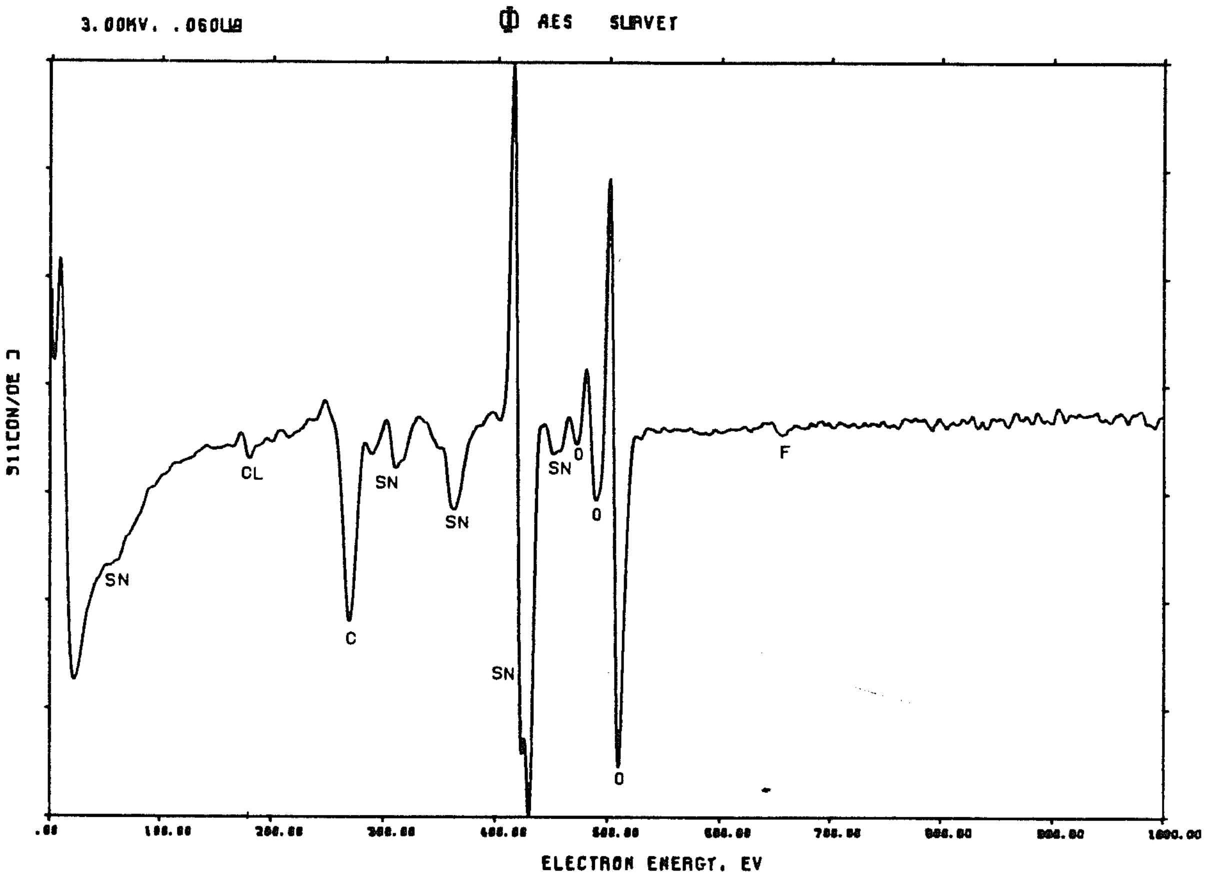

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Fig. 5a. 5b follows.

Fig. 5 (a) Auger electron spectroscopy of SnO_2:F heat mirror film showing typical composition at the surface of the coating. (b) Sputter depth chemical profile, showing the uniformity in composition throughout the film. Sputter rate is about 400A/min.

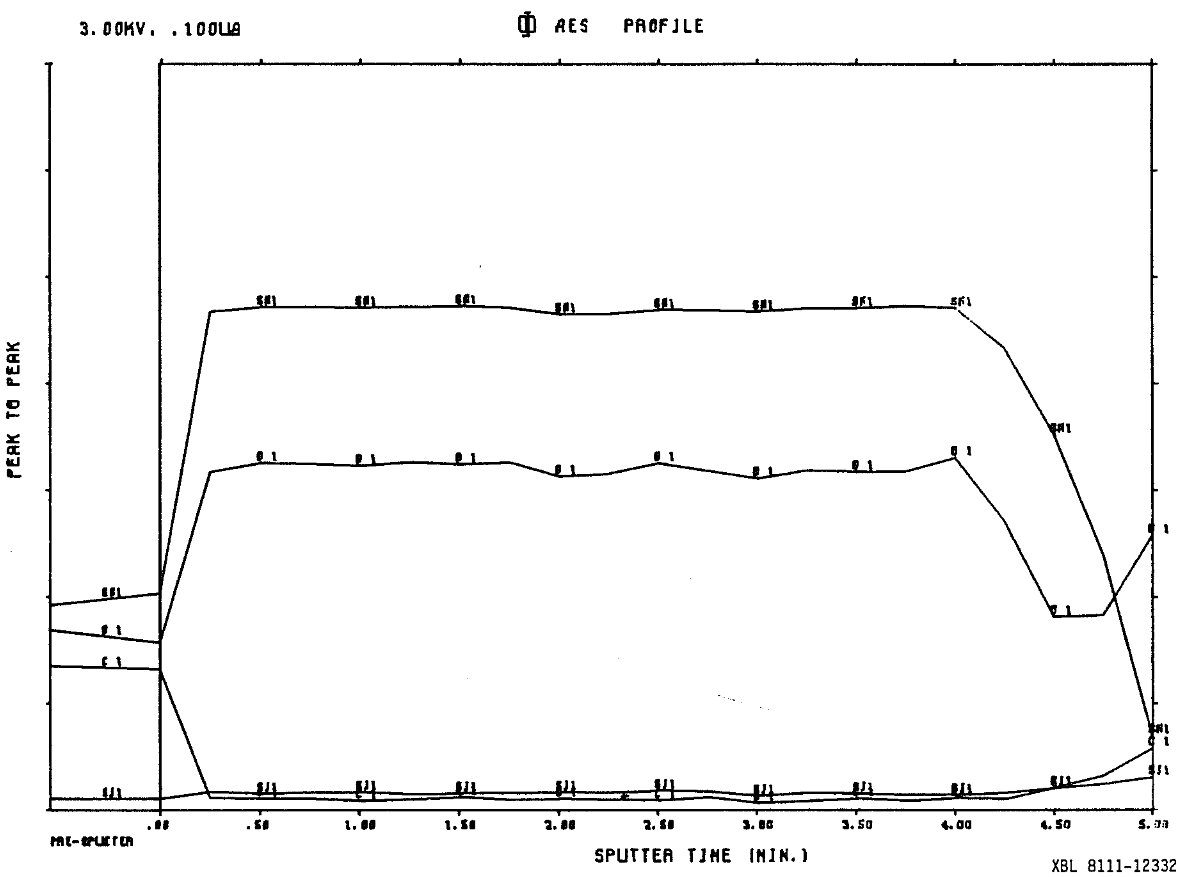

Fig. 5b. Fig. 5a plus caption on previous page.

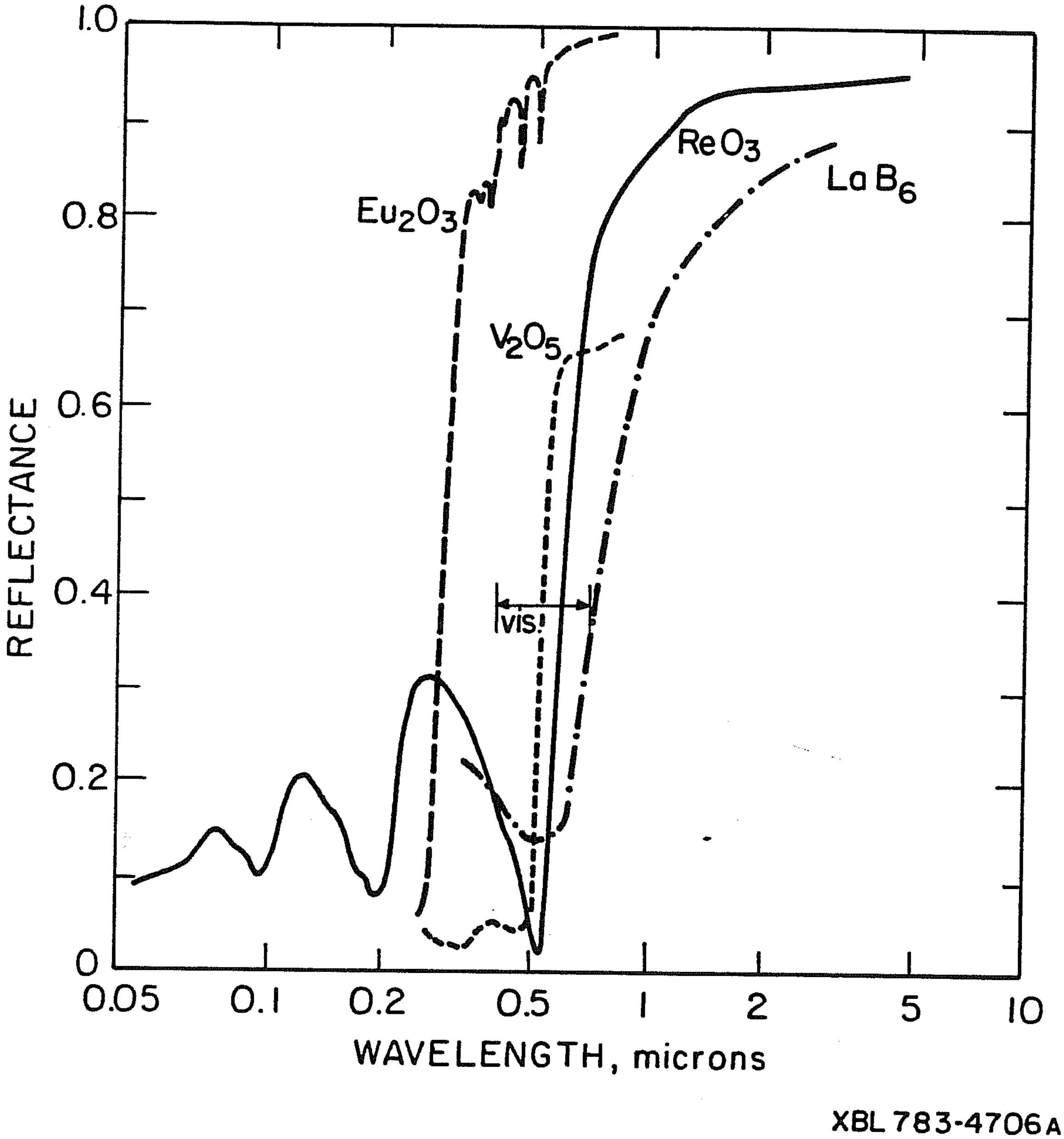

Fig. 6 Spectral reflectance of various oxides showing intrinsic selectivity for dieuropium trioxide, lanthanum hexaboride, rhenium trioxide (single crystal), and divanadium pentaboriae.

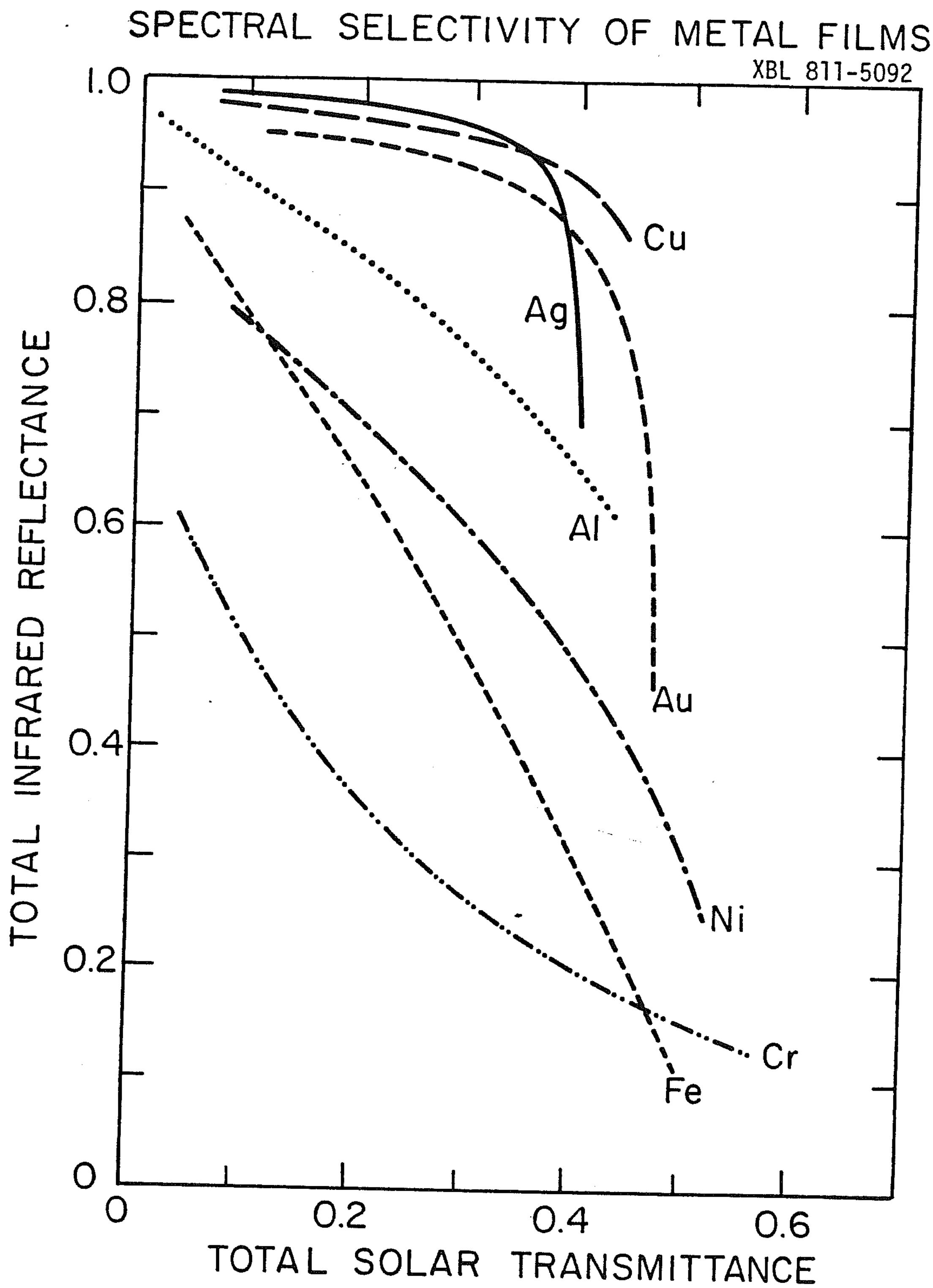

Fig. 7 Integrated infrared reflectance (room temperature) as a function of transmitted total solar radiation for thin metal films of various thicknesses.[16] For Au, Fe, Cr films, thicknesses range from 50–300 Å; for Ni and Al films from 25–2000 Å; and for Ag to Cu films from 90–400 Å.

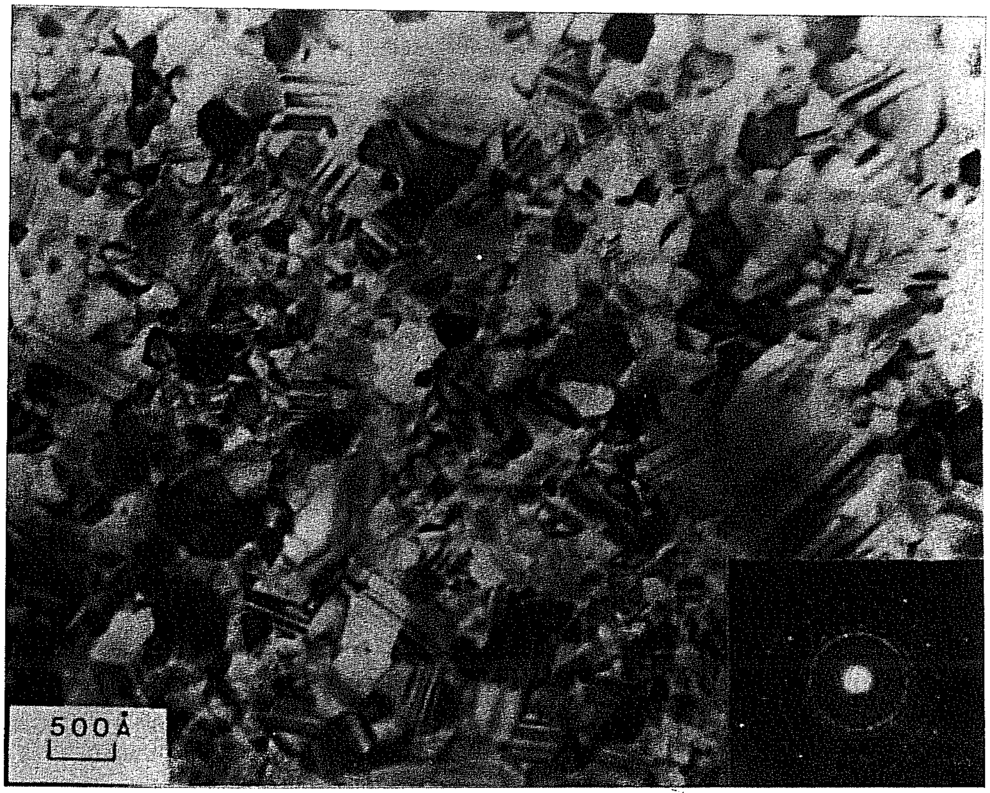

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Fig. 8 Transmission electron micrograph of the typical silver layer microstructure in 300 Å Al_2O_3/125 Å Ag on polyethylene terephthalate (polyester) substrate. This assembly is a prototype infrared reflector or heat mirror. The micrograph was taken at 100 kV in the bright field mode. The polycrystalline nature of the film is noted in both the micrograph and inset diffraction pattern.